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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

THE DETERMINATION OF CADMIUM IN CADMIUM-TIN ALLOYS

An oscillo-polarographic method

by

V. VERDINGH and H. CUYVERS

1967

Joint Nuclear Research Center
Geel Establishment - Belgium

Central Bureau for Nuclear Measurements - CBNM

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Brussels, July 1967 - 12 Pages - 2 Figures - FB 25

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SUMMARY

A simple polarographic method that allows the determination of Cd in Cd - Sn alloys is described. Sn is removed by treatment of the Cd - Sn solution with a mixture of HBr - Br_2. Small amounts of Sn reduce the height of the Cd peak. Knowing the Sn peak height a correction can be applied. 1N HC was chosen as an indifferent electrolyte. The coefficient of variation of the method is less than 1 %.

THE DETERMINATION OF CADMIUM IN CADMIUM - TIN ALLOYS

An oscillo-polarographic method(*)

1. Introduction

For the analysis of Cd - Sn alloys, used as activation detector for neutron flux measurements, a rapid polarographic method for the determination of Cd was needed.

The Cd content was of the order of 2 - 3 %.

The direct determination of Cd in the presence of large quantities of Sn is impossible because the half-wave potentials are to similar.

($E_{1/2}$ for Cd in 1M HCl = -0.64 for Sn in 1M HCl-0.47 S.C.E)

Sn has to be removed before the determination of Cd.

Sn was volatilized with a HBr - Br_2 mixture recommended by [2].

The Cd determination itself can be done in a variety of electrolytes [1], [4].

2. Experimental

Apparatus: A Southern A 1660 Davis Differential Cathode Ray polarograph was used. The potentials were measured versus a mercury pool anode. Some modifications of the apparatus are described in a previous publication [3].

2.1. Reagents

Cd : hyper pure : 99.999 % U.C.B. nr. 5417

Sn : hyper pure : 99.999 % U.C.B.

HCl Merck pro analysi

Merck titrisol

HBr Merck pro analysi

Br_2 Merck pro analysi

HNO_3 Merck supra pure

H_2O doubly distilled

(*) Manuscript received on May 23, 1967.

2.2. Preparation of solutions

2.2.1. Cadmium standard solution

About 500 mg Cd were dissolved in 100 ml conc. HCl + 1 ml conc. HNO_3. The solution was quantitatively transferred to a weighed 500 ml flask, diluted and weighed.
From this solution, reference solutions were prepared by weighing. Corrections for buoyancy were made for all weighing operations.

2.2.2. Sn solution

About 5.5 g Sn were dissolved in 20 ml conc. HNO_3 + 100 ml conc. HCl; after dissolution 40 ml conc. HCl were added and the volume was made up to 1000 ml in a volumetric flask.

2.2.3. HBr - Br mixture

50 ml HBr 40 % and 10 ml Br_2 were mixed in a 100 ml flask.

2.2.4. Cadmium solutions

Weighed portions of about 10 - 12 g Cd-stock solution were transferred to 250 ml beakers. For the Cd - Sn solutions, 30 ml Sn-stock solution was added.
After treatment with a HBr - Br_2 mixture, the residue was dissolved in 1 N HCl and quantitatively transferred to 100 ml flasks, diluted with 1 N HCl and weighed.

2.2.5. Sample solutions

About 180 mg of the Cd - Sn alloy were dissolved in 5 ml conc. HCl and 1 ml conc. HNO_3. After treatment with the HBr - Br_2 mixture the residue was dissolved

in 1 N HCl, quantitatively transferred to a 100 ml flask, diluted with 1 N HCl and weighed.

2.3. Removing of Sn

Cd can be determined in the presence of 2 % of tin. In the presence of larger quantities of Sn the Sn has to be removed until a concentration smaller than 10 % is reached.
A correction can be applied for the influence of the remaining Sn on the Cd peak (see 3.2.).
The Cd - Sn solutions were treated three times with 5 ml HBr - Br_2 mixture and carefully evaporated to dryness on a sand bath at a temperature of about 150°C.
The Sn is removed nearly quantitatively.
The influence of the remaining Sn on the Cd peak height after three evaporations is less than 1 % on the Cd content. A correction for this effect can be made. (see paragraph 3.2.).

2.4. Method

5 ml of the sample or calibration solution were brought into a cell and deaerated for 10 minutes with high purity nitrogen. "Slope compensation" and "condensor compensation" were used.
The start potential was about - 0.380 V. The peak potential for Cd lies at about - 0.670 Volt versus Hg-pool anode. In order to improve the reproducibility of the method, at least four or five cell-fillings were made from each solution. Each cell-filling was measured 11 times.
The mean of these measurements was used for further calculations.

3. Results

3.1. Calibration factor for Cd (C.F.)

The calibration factor for Cd is derived from measurements of pure Cd-reference solutions without treatment with the HBr - Br_2 mixture. It is the number of scale divisions at maximum sensitivity divided by the concentration of Cd given in µg/g solution.

C.F. = 1680 **S.D.** (scale divisions)/µg Cd/g solution

This value is used as a reference throughout the whole study. All peak heights were normalised to this value, even when changing capillary characteristics. The calibration factor of Sn is derived from measured Sn peak heights in presence of Cd (see 3.2.).

C.F. $\simeq$ 380 S.D./µg Sn/g solution

At concentrations of less than 10 % Sn (with respect to the Sn - Cd content) the reproducibility on the Sn peak height reading is about 20 %. Because the correction factor for influence of Sn on the Cd peak height is less than 1.010, a reproducibility of 20 % on this factor lies within the reproducibility of the method.

3.2. Influence of Sn on the Cd peak height

Solutions with known concentration ratio of Cd and Sn were measured. The decrease of the Cd peak height is proportional to the height of the Sn peak.

Calc.concentration in µg/g sol.		% Sn in Cd+Sn	Peak height (S.D.)		Found conc. µgCd/g sol.	Deviation from the calc.value (µg Cd/g sol.)
Cd	Sn		Cd	Sn		
80.43	0	0	135,100	0	80.43	- 0.00
80.43	9.10	10.20	134,300	3,500	79.94	- 0.49
80.43	22.75	22.00	130,400	8,700	77.62	- 2.81
80.43	45.50	36.10	125,800	17,500	74.88	- 5.55

A correction factor on the Cd peak height, proportional to the Sn peak height, can be applied.

Sn peak height S.D.	Correction factor for the Cd peak height
0	1.000
3,500	1.006
8,700	1.036
17,500	1.074

These values are illustrated in fig. 1. By extrapolation of the curve for lower Sn concentrations (after treatment with the HBr - B_2 mixture) one obtains another curve, fig. 2., from which the correction factor can be read. Working under normal conditions the correction factor to be applied is smaller than 1.010.

3.3. Analysis of Cd - Sn solutions after treatment with the HBr - Br_2 mixture

In all solutions the remaining Sn peak height was about 1500 S.D. (± 20 %). The correction factor for 1500 S.D. Sn is 1.0062.

Peak height Cd(SD) measured	Corrected peak height Cd(SD)	Calc.conc. Cd in µg/g solution	Found conc. Cd in µg/g solution	Deviation from the calc.value µgCd/gsol.
81,400	81,950	48.67	48.76	+ 0.10
81,600	82,150	48.97	48.88	- 0.09
84,350	84,900	50.79	50.53	- 0.26
72,550	73,000	43.87	43.51	- 0.36
82,300	82,850	49.21	49.31	+ 0.10
85,050	85,600	50.59	50.94	+ 0.35
79,500	80,000	47.32	47.68	+ 0.36
40,700	91,300	53.73	54.35	+ 0.62
84,300	84,850	50.67	50.18	- 0.49
84,200	84,200	50.65	50.25	- 0.40
72,500	72,500	43.19	43.19	0.00

The last two solutions were pure Cd solutions without Sn, but also treated with the HBr - Br mixture.

The coefficient of variation for this series of measurements $S/\bar{x}$ = 0.61 %.

3.4. Analysis of Cd - Sn alloys

From each sample three solutions were made and each solution was measured 3 times. In all solutions the remaining Sn peak height was of the order of 1000 S.D. The correction factor for 1000 S.D. Sn is 1.0042 (see 3.2.).

Sample	Cd peak height S.D.meas.	Cd peak height S.D.corr.	Weight sample g	Weight sol. g	% Cd in Cd-Sn
Tp 326 R	87,450	87,850	0.19835	102.0410	2.731
	87,900	88,300			2.744
	88,000	88,400			2.747
	85,050	85,450	0.19215	101.6329	2.730
	85,000	85,400			2.729
	84,700	85,100			2.719
	82,500	82,850	0.18830	102.5136	2.726
	82,650	83,000			2.731
	82,600	82,950			2.730
$\bar{x}$ = 2.732 $S/_{\bar{x}}$ = 0.32 %					
Tp 326 M	79,050	79,400	0.17805	101.4835	2.737
	79,200	79,550			2.742
	76,900	79,250			2.732
	85,300	85,700	0.19322	101.5378	2.721
	85,300	85,700			2.721
	85,500	85,900			2.727
	82,700	83,050	0.18540	101.4326	2.739
	82,500	82,850			2.732
	83,000	83,350			2.748
$\bar{x}$ = 2.733 $S/_{\bar{x}}$ = 0.34 %					

Acknowledgements

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4. References

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[2] A.S.T.M. Methods of Chemical Analysis of Metals 1946, p. 239

[3] V. Verdingh, Z. Anal. Chem. Bd. 220 Band 3, Heft 1966.

[4] V. Verdingh - M. Van Bouwel - unpublished.

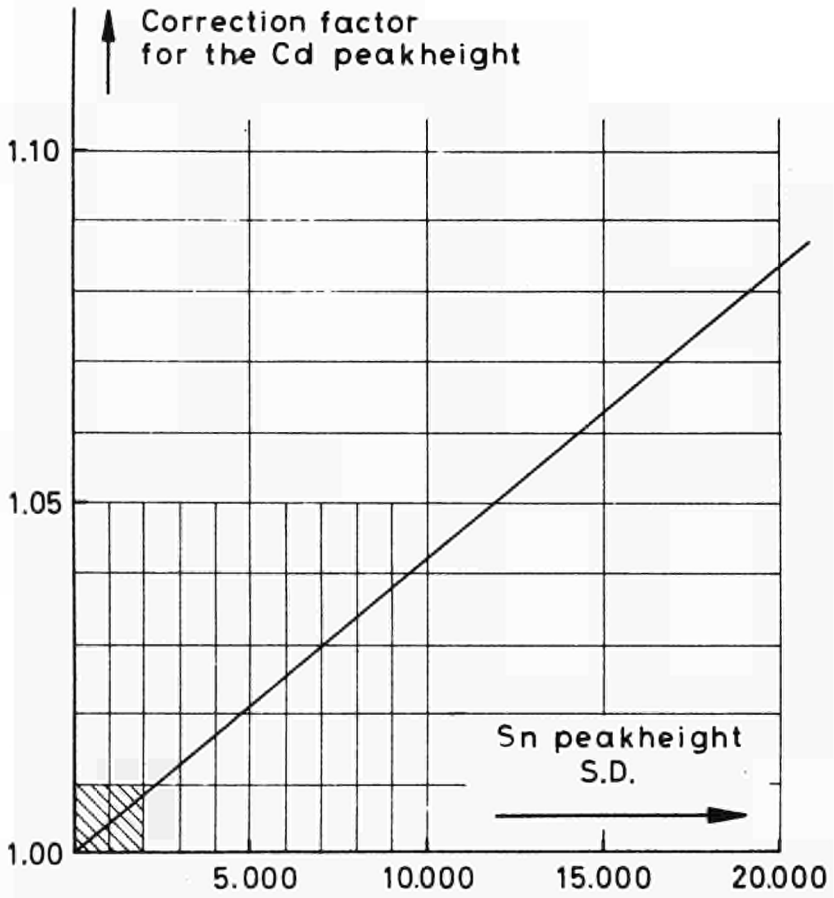

Correction factor
for the Cd peakheight
1.10
1.05
1.00
5.000
10.000
15.000
20.000
Sn peakheight
S.D.

fig.1

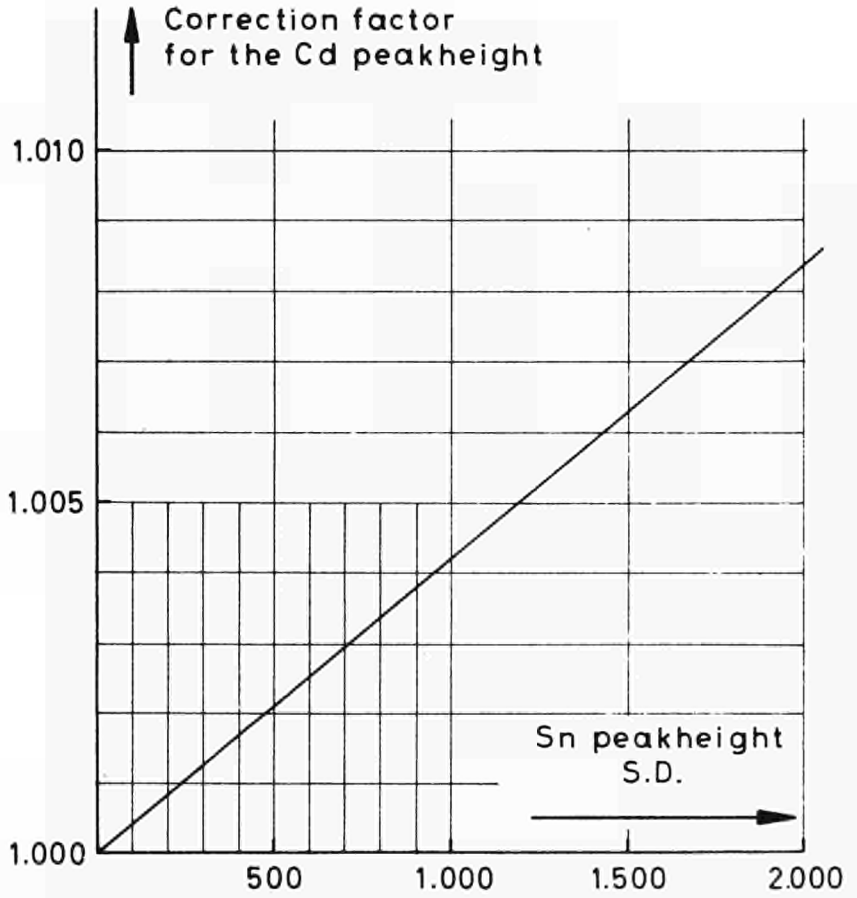
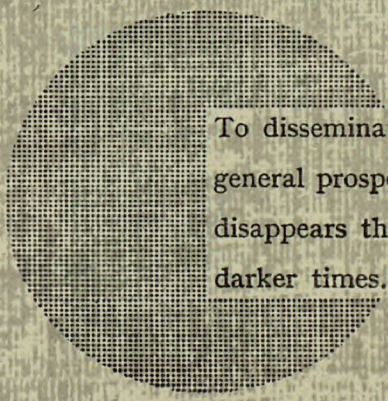

Correction factor
for the Cd peakheight
1.010
1.005
1.000
500
1.000
1.500
2.000
Sn peakheight
S.D.

fig.2



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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